

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



AG

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C10G 27/12	A1	(11) International Publication Number: WO 00/47696 (43) International Publication Date: 17 August 2000 (17.08.00)
(21) International Application Number: PCT/GB00/00117 (22) International Filing Date: 19 January 2000 (19.01.00) (30) Priority Data: 9903164.3 15 February 1999 (15.02.99) GB (71) Applicant (for all designated States except US): IMPERIAL CHEMICAL INDUSTRIES PLC (GB/GB); Imperial Chemical House, Millbank, London SW1P 3JF (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): ABBOTT, Peter, Edward, James (GB/GB); Glebe House, Muirfield Road, Eaglescliffe, Cleveland TS16 9EJ (GB). HANCOCK, Frederick, Ernest (GB/GB); 12 Ashville Avenue, Norton, Stockton on Tees, Cleveland TS20 1PS (GB). (74) Agents: GRATWICK, Christopher et al.; Syntex Intellectual Property Department, Building N, Room 101, Chilton Site, P.O. Box 1, Belasis Avenue, Billingham, Cleveland TS23 1LB (GB).		(81) Designated States: AU, BR, CA, CN, ID, IN, JP, KR, MX, SG, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.
(54) Title: SULPHUR REMOVAL (57) Abstract Sulphur compounds are removed from a liquid FCC gasoline stream by contact with a tertiary hydroperoxide with a catalyst effective to catalyse the reaction of tertiary hydroperoxides with sulphur compounds, whereby the sulphur compounds are converted to higher boiling point sulphur compounds. A higher boiling point fraction containing the higher boiling point sulphur compounds is subsequently separated from the hydrocarbon stream. Before separation of the higher boiling fraction, preferably residual hydroperoxide is decomposed catalytically using e.g. a nickel catalyst. The hydroperoxide may be made in situ by passing the FCC stream, which will contain a proportion of isoparaffins, and an oxygen-containing gas, e.g. air, over a catalyst such as alkalised alumina.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Sulphur removal

This invention relates to sulphur removal and in particular to the removal of sulphur compounds from liquid hydrocarbons, particularly gasoline FCC fractions produced by cracking naphtha. Such FCC fractions generally have an atmospheric pressure boiling range of up to 220°C and generally contain hydrocarbons containing 5 to 12 carbon atoms, in particular paraffins, olefins, cycloparaffins and aromatic hydrocarbons. The olefin content is usually at least 20% on a molar basis. Unfortunately, the FCC fractions generally also contain sulphur compounds, in particular mercaptans and thiophenic compounds.

There is growing environmental and legislative pressure on reducing the sulphur compound content of gasoline.

One known method is hydro-treating wherein the hydrocarbon is reacted with hydrogen in the presence of a suitable catalyst, often a nickel or cobalt molybdate, so the sulphur compounds are hydrogenated to form hydrogen sulphide. The hydrogen sulphide may then be removed by absorption in a regenerable wash system, e.g. amine scrubbing. However hydro-treating processes are liable to effect hydrogenation of valuable components such as aromatics or olefins in the hydrocarbon stream. This leads to a reduction in the octane number of the gasoline, which is a disadvantage with respect to its performance.

It has been proposed in US 5318690 to overcome this problem by fractionating a catalytically cracked naphtha to give a light and a heavy fraction. The light fraction, which contains the olefin components and the low boiling sulphur compounds such as mercaptans, is subjected to an oxidative sweetening process, while the heavy fraction containing higher sulphur compounds such as thiophenes is subjected to hydro-desulphurisation and then the hydro-desulphurised higher fraction is subjected to a controlled cracking to increase the octane rating thereof. Since the cracking produces olefins which may combine with the hydrogen sulphide produced in the hydro-desulphurisation stage, the product is subjected to a further hydro-desulphurisation step and then combined with the sweetened light fraction after removal of the sulphides and disulphides therefrom.

The oxidative sweetening process of FCC gasoline fractions is well known, see for example US 4206043, GB 2071134 and US 4574121, and comprises contacting the liquid fraction with an oxygen-containing gas, e.g. air, in the presence of a suitable catalyst, e.g. cobalt phthalocyanine, often dispersed in an aqueous caustic solution. As a result of the oxidative sweetening, the mercaptans are converted to sulphides and/or di-sulphides. However this oxidative sweetening does not effect oxidation of the thiophenic sulphur compounds.

It is also known that sulphur compounds in hydrocarbons can be oxidised to sulfoxides and/or sulphones. Thus GB 2262942 and EP 0565324 describe the non-catalytic oxidative

treatment of both light and heavy liquid hydrocarbons, for example ranging from naphtha, through gasoline, kerosene and gas oil to heavy fuel oils, containing sulphur compounds to give the corresponding sulfoxide and/or sulphone having increased boiling points compared to the unoxidised sulphur compounds and suggest that the sulphur compounds may be separated by
5 subjecting the hydrocarbon to distillation leaving the oxidised sulphur compound as a component of the distillation residue. US 3816301 discloses that thiophenic sulphur compounds in heavy hydrocarbons can be oxidised using hydroperoxides, for example tertiary butyl hydroperoxide formed by the oxidation of isobutane with a gas containing free oxygen.

We have found that, surprisingly, hydroperoxides can be used to oxidise the sulphur
10 compounds in FCC streams to higher boiling compounds with minimal oxidation of the aromatics and olefinic components thereof. Hereinafter, boiling points refer to the boiling points at atmospheric pressure. For example dimethyl sulphide has a boiling point of about 38°C whereas the oxidation product, dimethyl sulfoxide, has a boiling point of 190°C and the further oxidation product, dimethyl sulphone, has a boiling point of 238°C. Likewise thiophene has a
15 boiling point of 84°C while thiophene sulfoxide has a boiling point of about 215-220°C.

We have therefore realised that the process of US 5318690 may be simplified by oxidising the FCC stream under conditions effective to convert the sulphur compounds to sulfoxides or sulphones with minimal oxidation of the olefins present and the subjecting the treated FCC stream to fractional distillation to separate the lighter components of the FCC stream, including
20 the olefin components, as a gasoline fraction having a greatly reduced sulphur content, leaving a small higher boiling fraction containing the oxidised sulphur compounds. If desired, as described in US 5318690 this higher boiling fraction may be desulphurised by conventional techniques such as hydro-desulphurisation and then mixed with the lighter fraction. Alternatively the higher boiling fraction, after hydro-desulphurisation if desired, can be added to the heavy FCC fraction
25 (boiling range typically >200°C), which may be hydrotreated before being added to the diesel pool.

Accordingly the present invention provides a process for the removal of sulphur compounds from a liquid hydrocarbon FCC stream containing olefins and thiophenic sulphur compounds comprising contacting said hydrocarbon stream and a tertiary hydroperoxide with a
30 catalyst effective to catalyse the reaction of tertiary hydroperoxides with sulphur compounds, whereby the sulphur compounds are converted to higher boiling point sulphur compounds and thereafter separating a higher boiling point fraction containing said higher boiling point sulphur compounds from said hydrocarbon stream.

Suitable catalysts can be constructed from the Group IV, VI and VIII metals. Examples of
35 such catalysts include titanium silicate or metallo-phthalocyanine compounds (supported or

unsupported), for example cobalt phthalocyanine which may be used as such, i.e. unsupported, or sulphonated on the phthalocyanine ring to give a water soluble derivative which is used to impregnate a suitable support to form a supported catalyst. The catalyst is desirably selective for the oxidation of sulphur species without loss of hydroperoxide to oxygen gas and the corresponding alcohol. The reaction is preferably effected with the catalyst in the form of a fixed bed through which the hydrocarbon stream, in the liquid state, and containing the hydroperoxide, is passed. Since the hydroperoxides tend to decompose at relatively low temperatures, the reaction is preferably effected adiabatically with the hydrocarbon stream being fed to the catalyst at a temperature in the range 20 to 80°C. The amount of hydroperoxide required will normally depend on the amount and nature of the sulphur compounds. Thus generally there should be at least one mole of hydroperoxide per mole of sulphur compound. An excess of hydroperoxide should normally be employed.

The tertiary hydroperoxide may be formed by reacting an isoparaffin, e.g. isobutane (2-methyl propane) or isopentane (2-methyl butane) with a gas containing free oxygen, preferably air, in the presence of a catalyst effective to catalyse the oxidation of isoparaffins to tertiary hydroperoxides. Suitable catalysts include basic catalysts such as alumina impregnated with potassium hydroxide. The hydroperoxide, preferably without separation thereof from any residual isoparaffin, may then be added to the hydrocarbon stream to be treated. Alternatively, and preferably, the hydroperoxide may be made in situ. Thus the FCC hydrocarbon stream itself will normally contain a proportion of isoparaffins. Typically FCC streams contain 5-15% by weight of pentanes of which 65-85% is isopentane (2-methyl butane). Alternatively an isoparaffin stream may be added to the hydrocarbon stream to be treated. By passing the hydrocarbon stream containing the isoparaffin over a basic catalyst as aforesaid while bubbling an oxygen-containing gas such as air through the hydrocarbon, the tertiary hydroperoxide may be formed. Since the reaction forming the hydroperoxide is exothermic but the peroxides decompose at relatively low temperatures, the reaction is preferably effected adiabatically at relatively low temperatures with the hydrocarbon stream being fed to the catalyst at a temperature in the range 20-80°C. The remainder of the hydrocarbon stream acts as a diluent to keep the temperature rise resulting from the exothermic reaction to a minimum. The operation of the formation of the hydroperoxide at low temperatures is desirable to avoid side reactions, e.g. oxidation of other components of the hydrocarbon stream. The reaction is conveniently effected using a fixed bed of the catalyst with the hydrocarbon flowing, in the liquid state, down through the catalyst while air is injected into the liquid beneath the catalyst and flows upwards counter-current to the hydrocarbon liquid. The air is likewise preferably fed at a temperature in the range 20-80°C.

In another possible arrangement, the system is operated at an elevated pressure, for example 10 to 20 bar abs. and compressed air is injected into, and dissolves in, the pressurised liquid hydrocarbon and the resulting solution is then passed through the catalyst bed.

As indicated above, an excess of the hydroperoxide should normally be employed in the sulphur compound oxidation stage. Hence the amount of oxygen-containing gas that needs to be introduced to produce the hydroperoxide will depend on the amount and nature of the sulphur compounds and the efficiency with which the oxygen-containing gas is utilised to form the hydroperoxides. Normally the amount of isoparaffins present will be far greater, in molar terms, than the amount of hydroperoxide required in the sulphur compound oxidation step, even after allowing for an excess of the hydroperoxide in that step. Hence the amount of oxygen-containing gas required is normally insufficient to oxidise all the isoparaffins present. However, there will normally be a small excess of oxygen-containing gas, e.g. air, leaving the hydroperoxide formation stage. This gas can be bled off and used as part of combustion air in an associated process employed in the production or further treatment of the hydrocarbon stream.

The formation of the hydroperoxide and oxidation of the sulphur compounds may be effected in different vessels, but in a preferred process, they are effected in a single vessel with the sulphur compound oxidation catalyst preferably disposed as a fixed bed beneath a fixed bed of the hydroperoxide formation catalyst with the hydrocarbon stream flowing down through the beds and with the oxygen-containing gas injected between the beds. However in some cases it may be more convenient, where both catalyst beds are located in a single column or vessel, to inject the oxygen-containing gas at a location beneath the sulphur compound oxidation catalyst. In another alternative a single bed consisting of a mixture of the two catalysts may be employed.

Where the beds of catalyst are disposed are disposed in a single vessel or column, it is generally convenient to operate both stages at essentially the same pressure and temperature so that there is no need for heating or cooling and/or compression or expansion between the stages. The pressure is preferably in the range 1 to 20 bar abs., especially in the range 1 to 15 bar abs.

After the sulphur compound oxidation step, the mixture will normally contain some residual hydroperoxide. The excess is preferably decomposed before separation of the oxidised sulphur compounds. The excess of hydroperoxide may be decomposed by heating the mixture, e.g. to a temperature above 100°C, but this is less preferred as the residual hydroperoxide may tend to react with other components, e.g. aromatic or olefinic components, of the hydrocarbon stream which not only may result in loss of desired products, but also may produce gums or other undesirable compounds.

In a preferred arrangement the residual hydroperoxide may be decomposed by passing the hydrocarbon stream over a suitable hydroperoxide decomposition catalyst, for example a catalyst comprising oxides of at least one metal selected from iron, nickel, cobalt and copper preferably nickel, for example in the form of porous shaped particles containing 10 to 70% by weight of nickel oxide and a calcium aluminate cement as a binder. Such catalysts decompose the residual hydroperoxide with the formation of oxygen. The catalyst used for the decomposition of the residual hydroperoxide may be disposed as a fixed bed in a separate vessel but preferably is disposed in the same vessel as the sulphur compound oxidation catalyst, especially in a column beneath the sulphur oxidation catalyst down through which the hydrocarbon stream is passing. In this way the oxygen formed by decomposition of the residual hydroperoxide can flow up through the sulphur compound oxidation bed and augment the oxygen-containing gas used to form the hydroperoxide.

Catalytic decomposition of the residual hydroperoxide is preferably effected at substantially the same temperature and pressure as was employed for the sulphur compound oxidation step.

The liquid hourly space velocity through each catalyst bed is typically in the range 1 to 10 h^{-1} .

After the sulphur compound oxidation step, and preferably after a residual hydroperoxide decomposition step, the hydrocarbon stream is subjected to a separation process, e.g. fractional distillation, to separate a higher boiling point stream containing the oxidised sulphur compounds. As indicated above, the higher boiling stream may be added to the heavy FCC fraction. The oxidised sulphur compounds can be removed from this stream by the conventional hydrotreating employed for sulphur reduction of diesel. Alternatively, the higher boiling stream, which will be largely free from olefinic compounds, may be subjected to conventional sulphur removal, e.g. hydrotreatment and sulphur absorption and then returned to the lower boiling fraction or otherwise used.

The reaction of the hydroperoxides with the sulphur compounds, and the subsequent decomposition of residual hydroperoxides, gives rise to alcohols. These will normally have boiling points within the range of the lighter fraction and so will form part of the treated hydrocarbon product stream. However since they are oxygenates, their presence will have the benefit of octane enhancement and improve the flame burning characteristics of the hydrocarbon product stream, and so will generally not need to be separated.

The invention is illustrated with reference to the accompanying drawing which is a diagrammatic flowsheet of one embodiment of the process.

In the drawing a column 10 is provided with three catalyst beds: an upper bed 11 of a particulate hydroperoxide formation catalyst, e.g. alkalised alumina, a middle bed 12 of a particulate sulphur-compound oxidation catalyst, e.g. a titanium silicalite, and a lower bed 13 of a particulate hydroperoxide decomposition catalyst, e.g. nickel oxide supported on alumina or calcium aluminate. A FCC gasoline stream containing hydrocarbons having at least 5 carbon atoms and containing a proportion of isopentane, is fed to the upper end of the column 10 via a line 14. Typically the FCC stream is fed at a pressure in the range 2 to 5 bar abs., and at a temperature in the range 20 to 70°C. Air is fed via line 15 to a compressor 16 and thence via a cooler 17 and line 18 to a location between the beds 11 and 12. The air passes up through the catalyst bed 11 counter-current to the flow of the hydrocarbon stream and effects oxidation of some of the isoparaffins in the FCC stream to hydroperoxides. The excess of air is exhausted from the top of the column 10 via line 19 and is used elsewhere as combustion air. The FCC stream, containing the sulphur compounds and the hydroperoxides, then passes down through the sulphur-compound oxidation catalyst bed 12 wherein the hydroperoxides oxidise the sulphur compounds to higher boiling point compounds. The hydrocarbon stream then passes down through the hydroperoxide decomposition bed 13 wherein the residual hydroperoxides are decomposed: oxygen released by decomposition of the residual hydroperoxides passes up through the bed 12 and augments the air supplied via line 18.

The hydrocarbon stream, containing the oxidised sulphur compounds, then leaves the bottom of the column via line 20 and is then fed to a fractional distillation unit (not shown). A high boiling point fraction, containing the oxidised sulphur compounds, is separated in the distillation unit. Typically about 5-15% of the product stream 20 will be separated as the high boiling point stream in the subsequent fractional distillation. This separated stream will contain little olefinic components and so the octane rating of the light fraction will not be significantly reduced.

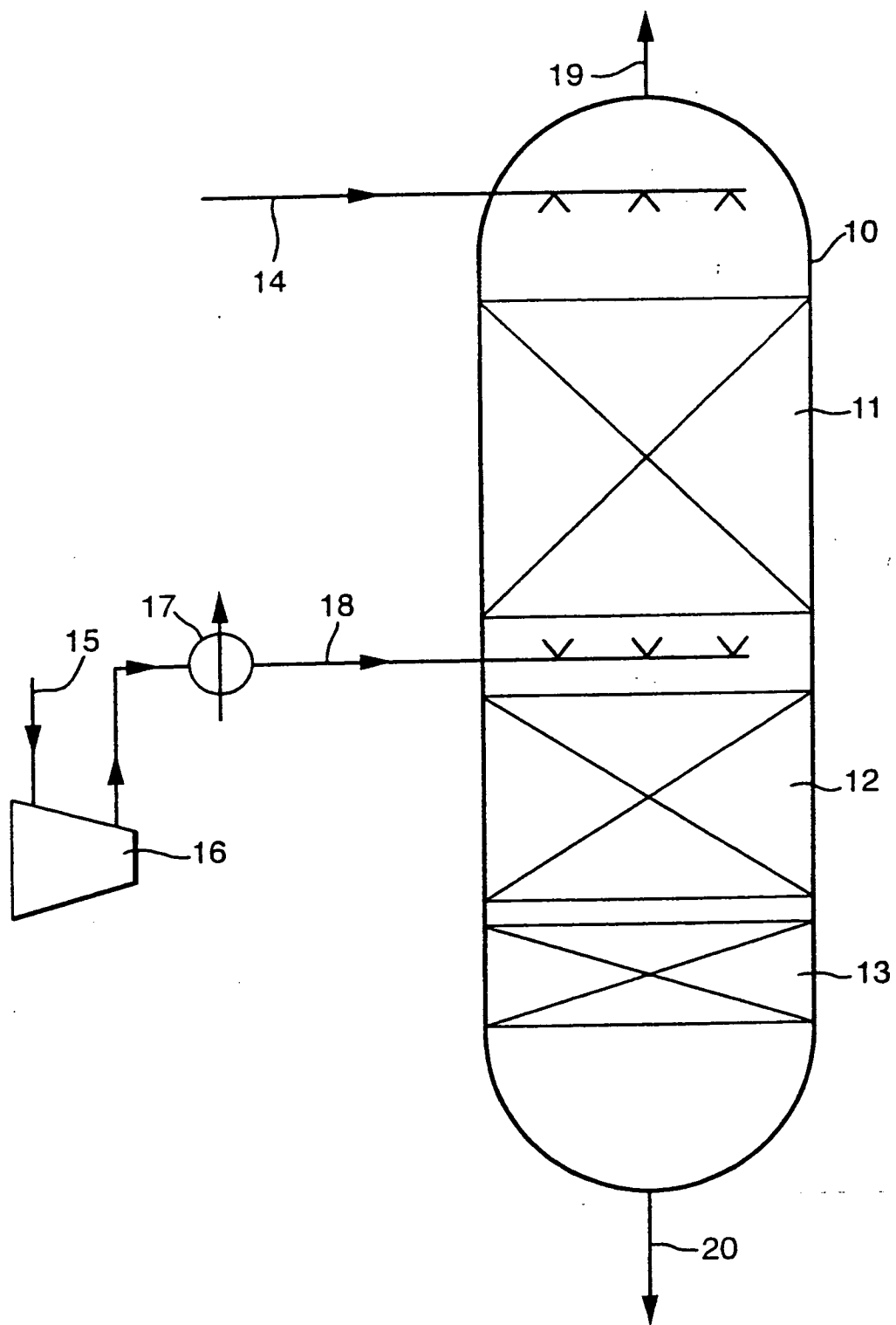
The following calculated example illustrates one embodiment of the invention using the flowsheet of the drawing to treat about 2200 metric tons per day (hereinafter tpd) of an FCC 5+ gasoline fraction containing about 0.6 tpd of sulphur as mercaptans and about 4.5 tpd of sulphur as thiophenic and similar compounds. The process is operated adiabatically with the air and gasoline fraction being fed to the column at a temperature of 40°C and the gasoline fed at a pressure of 3 bar abs. It is assumed that only the isopentane reacts to form hydroperoxides, and that the mercaptan sulphur is oxidised to sulphonic acids while the thiophenic sulphur is oxidised to sulfoxides. The following table shows the calculated flow rates and temperatures.

	Stream flow rate (kmol/h)					
	14	18	liquid ex bed 11	19	liquid ex bed 12	20
2-methyl butane	50		40		40	40
Other pentanes	100		100		100	100
C5+ olefins	325		325		325	325
C6+ paraffins	270		270		270	270
C6+ naphthenes	85		85		85	85
C6+ aromatics	155		155		155	155
Mercaptan sulphur	0.8		0.8		0	0
Thiophenic sulphur	5.8		5.8		0	0
Oxygen		12		3.8		
Nitrogen		45		45		
Hydroperoxide			10		1.8	0
Sulphoxides					5.8	5.8
Sulphonic acids					0.8	0.8
Pentanol					8.2	10
Total flow (kmol/h)	991.6	57	991.6	48.3	991.6	991.6
Total weight flow (kg/h)	91780	1650	92100	1410	92100	92071
Temperature (°C)	40	40	45	40	54	54

Claims

1. A process for the removal of sulphur compounds from a liquid hydrocarbon FCC stream containing olefins and thiophenic sulphur compounds comprising contacting said hydrocarbon stream and a tertiary hydroperoxide with a catalyst effective to catalyse the reaction of tertiary hydroperoxides with sulphur compounds, whereby the sulphur compounds are converted to higher boiling point sulphur compounds and thereafter separating a higher boiling point fraction containing said higher boiling point sulphur compounds from said hydrocarbon stream.
2. A process according to claim 1 wherein the reaction is effected adiabatically with the hydrocarbon stream being fed to the catalyst at a temperature in the range 20 to 80°C.
3. A process according to claim 1 or claim 2 wherein the FCC hydrocarbon stream contains at least one isoparaffin, and is contacted with a gas containing free oxygen in the presence of a catalyst effective to catalyse the oxidation of isoparaffins to tertiary hydroperoxides, whereby tertiary hydroperoxides are formed in said hydrocarbon stream and the hydrocarbon stream containing the hydroperoxides is contacted with the catalyst effective to catalyse the reaction of tertiary hydroperoxides with sulphur compounds.
4. A process according to claim 3 wherein the catalyst effective to catalyse the oxidation of isoparaffins to tertiary hydroperoxides is alumina impregnated with potassium hydroxide.
5. A process according to claim 3 or claim 4 wherein the sulphur compound oxidation catalyst is disposed as a fixed bed beneath a fixed bed of the hydroperoxide formation catalyst, the hydrocarbon stream is passed down through the beds and the oxygen-containing gas is injected between the beds.
6. A process according to claim 3 or claim 4 wherein the sulphur compound oxidation catalyst is disposed as a fixed bed beneath a fixed bed of the hydroperoxide formation catalyst, the hydrocarbon stream is passed down through the beds at a pressure in the range 10 to 20 bar abs. and the oxygen-containing gas is injected into the hydrocarbon stream before it enters the first bed.

7. A process according to claim 5 or claim 6 wherein the hydrocarbon stream and oxygen-containing gas are fed to the bed of hydroperoxide formation catalyst at temperatures in the range 20 to 80°C.
8. A process according to any one of claims 1 to 7 wherein, after passage through the bed of the catalyst effective to catalyse the reaction of tertiary hydroperoxides with sulphur compounds, residual hydroperoxide in the hydrocarbon stream is decomposed by passing the hydrocarbon stream over a hydroperoxide decomposition catalyst before the higher boiling point fraction containing the higher boiling point sulphur compounds is separated from the hydrocarbon stream.
9. A process according to claim 8 wherein the hydroperoxide decomposition catalyst comprises oxides of at least one metal selected from iron, nickel, cobalt and copper.
10. A process according to claim 8 or claim 9 wherein the hydroperoxide decomposition catalyst is disposed as a fixed bed beneath the catalyst effective to catalyse the reaction of tertiary hydroperoxides with sulphur compounds.



INTERNATIONAL SEARCH REPORT

Int. l. Application No

PCT/GB 00/00117

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10G27/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	GB 1 132 875 A (ESSO RESEARCH AND ENGINEERING CO) 6 November 1968 (1968-11-06)	1
Y	claim 1 page 2, line 21 - line 40 ---	1-3
X	US 3 816 301 A (ATLANTIC RICHFIELD CO) 11 June 1974 (1974-06-11) cited in the application claims 1,2,11 column 7, line 38 -column 8, line 37 ---	1,2
Y	GB 713 740 A (ANGLO IRANIAN OIL CO) 18 August 1954 (1954-08-18) claims 1,6 page 1, line 53 - line 57 page 1, line 81 - line 84 ---	1-3
	-/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

29 March 2000

Date of mailing of the international search report

07/04/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

De Herdt, 0

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/00117

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 115 382 A (BRITISH PETROLEUM CO PLC) 8 August 1984 (1984-08-08) claims 1,3,4,6,8-10 page 3, line 26 - line 33 page 4, line 14 - line 5 -----	1,3,8-10

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

page 2 of 2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/00117

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 1132875 A		DE 1545280 A FR 1472280 A NL 6602260 A US 3505210 A	27-11-1969 24-05-1967 24-08-1966 07-04-1970
US 3816301 A	11-06-1974	CA 1007253 A GB 1425850 A JP 49052803 A	22-03-1977 18-02-1976 22-05-1974
GB 713740 A		NONE	
EP 0115382 A	08-08-1984	AU 2416684 A CA 1202927 A WO 8402716 A JP 60500450 T NO 843369 A ZA 8400126 A	02-08-1984 08-04-1986 19-07-1984 04-04-1985 23-08-1984 28-08-1985

